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<b>(21) International Application Number:</b> PCT/US99/21710 <b>(22) International Filing Date:</b> 20 September 1999 (20.09.99) <b>(30) Priority Data:</b> 09/157,840                      21 September 1998 (21.09.98)      US 09/382,067                      24 August 1999 (24.08.99)        US <b>(71) Applicant:</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). <b>(72) Inventors:</b> LEE, Yann-Per; 6386 Kings Arms Way, Fairfield, OH 45014 (US). FRANCE, Paul, Amaat; 8375 Todd Creek Circle, West Chester, OH 45069 (US). RADOMYSEL- SKIY, Arseniy; Apartment 3, 2940 Portsmouth Avenue, Cincinnati, OH 45208 (US). <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		<b>(81) Designated States:</b> AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KR (Utility model), KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> DURABLY WETTABLE LIQUID PERVIOUS WEBS PREPARED USING A REMOTE PLASMA POLYMERIZATION PROCESS  <b>(57) Abstract</b>  Disclosed is a durably wettable, liquid pervious web that is particularly suitable as a topsheet for absorbent articles such as baby and adult diapers and feminine hygiene products. The durably wettable, liquid pervious web is derived from a polymeric film or nonwoven to which is applied a thin organic material onto at least one surface of the starting film or nonwoven. The thin organic coating is in the form of a polymer and is obtained by after-glow (or remote) plasma-induced polymerization of a polymerizable unsaturated compound, preferably a polymerizable vinyl or isopropenyl compound, under specific plasma conditions.		

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**DURABLY WETTABLE LIQUID PERVIOUS WEBS  
PREPARED USING A REMOTE PLASMA POLYMERIZATION PROCESS**

CROSS REFERENCE TO RELATED APPLICATIONS

This is a Continuation-in-Part of co-pending application Serial No. 09/157,840 filed September 29, 1998.

TECHNICAL FIELD

5           The present invention relates to a durably wettable, liquid pervious web that is particularly suitable as a topsheet for absorbent articles. More particularly, the invention relates to a polymeric film or nonwoven to which is applied a thin organic material onto at least one surface of the film or nonwoven. The thin organic coating is in the form of a polymer and is obtained by after-glow plasma-induced polymerization of a polymerizable unsaturated compound, preferably  
10 a polymerizable vinyl or isopropenyl compound, under specific plasma conditions. The invention further relates to a process for making the durably wettable liquid pervious web, and to articles containing the durably wettable, liquid pervious web as a topsheet.

BACKGROUND OF THE INVENTION

15           Polymeric and nonwoven webs are common components of disposable absorbant articles, dryer sheets and the like. More particularly, macroscopically expanded, three-dimensional, polymeric films have been utilized as topsheet materials for disposable absorbent articles. As used herein, the term "macroscopically expanded", when used to describe three-dimensional webs, refers to webs which have been caused to conform to the surface of a three-dimensional  
20 forming structure so that both surfaces thereof exhibit the three-dimensional pattern of the forming structure or webs that have an inherent three-dimensional pattern arising from their structure. Regardless of whether the three-dimensional pattern is inherent or generated by application of a forming process, the pattern is readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches. By  
25 way of contrast, the term "planar", when utilized herein to describe nonwovens and polymeric

films, refers to the overall condition of the web when viewed by the naked eye on a macroscopic scale. In this context "planar" webs may include webs having fine-scale surface aberrations on one or both sides, the surface aberrations not being readily visible to the naked eye when the perpendicular distance between the viewer's eye and the plane of the web is about 12 inches or greater.

One macroscopically expanded, three-dimensional apertured polymeric web which is particularly well suited to transferring liquid deposited on one surface thereof to its opposite surface and thereafter isolating the transferred liquid from a wearer's skin is disclosed in commonly assigned U.S. Patent No. 3,929,135 issued to Thompson on Dec. 30, 1975, the disclosure of which is incorporated by reference herein. Thompson describes a macroscopically expanded, three dimensional web (e.g., a topsheet) comprised of liquid impermeable material, but provided with a pattern of tapered capillaries, the capillaries having a base opening in the plane of the topsheet and an apex opening remote from the plane of the topsheet, the apex opening being in intimate contact with the absorbent pad utilized in the disposable absorbent article. The Thompson topsheet allows the free transfer of liquids from the wearer's body into the absorbent element of the device while inhibiting the reverse flow of these liquids. This provides a relatively much drier surface in contact with the user than had previously been obtainable. Another macroscopically expanded, three-dimensional apertured plastic web well suited for use as a topsheet on absorbent articles such as sanitary napkins is disclosed in commonly assigned U.S. Patent No. 4,342,314 issued to Radel et al. on Aug. 3, 1982, the patent being hereby incorporated by reference herein. The macroscopically expanded, three-dimensional plastic web disclosed in the Radel patent exhibits a fiber-like appearance and tactile impression which has been favorably received by consumers when used as a wearer contacting surface. According to the teachings of the commonly assigned patents to Thompson and to Radel, et al., plastic webs of the aforementioned type can be made by applying a pressure to the web while it is supported on a three-dimensional forming structure until the web is macroscopically expanded to comply with the three-dimensional cross-section of the forming structure on which it is supported. When aperturing of the macroscopically expanded, three-dimensional web is desired, the pressure differential is applied until such time as aperturing of the web in areas coinciding with the apertures in the forming structure has been completed.

A multi-phase, liquid-based process such as that described in U.S. Patent No. 4,609,518, issued September 2, 1986 to Curro et al. (hereafter referred to as "'518 patent"), the disclosure of which is incorporated herein by reference, was also developed to provide a film with very small and very large apertures immediately adjacent one another. As the patent discloses, the formation of the very small (including micro-sized) apertures in the direction opposite those formed for

large apertures hinders the ability of initially unabsorbed liquid from running off the web's surface. Thus, liquid not immediately transported through the large apertures is restrained from running off the web's surface, and is subsequently taken up through the larger apertures and is deposited in the article's core where the web is used as a topsheet material. These outwardly  
5 formed small apertures also reduce the level of web/skin contact and reduce the rigidity of the film, and thereby feel more comfortable to the user. Wearers have reported that such topsheets have a soft silky surface. Alternatively, the '518 patent discloses films where the very small apertures are formed in the same direction as the macro-apertures.

Regardless of the means employed for aperture formation, where a wettable film material  
10 is desired, the above references generally obtain such a structure by surface treating the naturally hydrophobic polymeric web with a wetting agent. Surface treatment is generally accomplished by either spraying surfactant onto the web's surface or by dipping the web in a surfactant-containing bath. Regardless of which of these methods is employed, surface treatment suffers from the inability to precisely control the location and level of treatment, as well as adverse effects caused  
15 by migration of significant amounts of surfactant into apertures and other components (e.g., absorbent core) when the web is used as a topsheet in an absorbent article. Surface treatment further suffers from the disadvantage that desirable wetting agents, or surfactants, tend to be washed off upon repeated exposure to such liquids. Thus, when used as a topsheet in an absorbent article, the treated webs lose their ability to transport liquid away from the skin and into  
20 the article's core after repeated wettings.

U.S. Patent No. 4,535,020, issued to Thomas et al. on August 13, 1985, addresses some of the problems associated with surface treating vacuum-formed apertured films by incorporating hydrophilic surfactant in the polymeric resin before extrusion for film formation (referred to herein as "resin incorporated surfactant", or "RIS"). (See also commonly assigned U.S. Patent  
25 Application Serial No. 08/713,377, filed September 13, 1996 by Y. P. Lee, et al.; U.S. Patent No. 4,923,914 to Nohr et al., issued May 8, 1990; U.S. Patent No. 5,057,262 to Nohr et al., issued October 15, 1991; U.S. Patent No. 5,120,888 to Nohr et al., issued June 9, 1992.) According to the teachings of Thomas, after extrusion of the resin/surfactant mixture, and subsequent formation of the apertures, the incompatible surfactant eventually blooms to the film's surface to provide a  
30 more durably wettable web. However, as with surface treatment, RIS suffers from some degree of surfactant wash-off during use and/or during manufacture, particularly if liquid pressure differentials are used to form the web's apertures. Also, hydrophilic webs formed using RIS techniques are not immediately wettable and, depending on the relationship between the resin and the surfactant and environmental conditions, may not become wettable for finite periods of time.  
35 Similarly, when such webs are used in absorbent articles, there will be some time delay before

surfactant (that is washed off during wear) is replenished at the web's surface.

In spite of the teachings of the related art, there remains a need for a durably wettable, liquid pervious web that offers improved durable wettability after the passage of time and/or after exposure to liquid insults. Such treated webs have particular suitability for use in disposable  
5 absorbent structures. There also remains the need for a process that provides such durably wettable web.

Accordingly, it is an object of the present invention to provide a durably wettable, liquid pervious web having improved durable wettability. This durable wettability is attained by applying a plasma-induced hydrophilic coating onto at least one surface of a starting web, to  
10 render the resulting treated web durably hydrophilic. In particular, the plasma-induced coating is attained using an "after-glow" or "remote" plasma polymerization process.

#### SUMMARY OF THE INVENTION

The present invention relates to a durably wettable, liquid pervious web that is particularly useful as a topsheet material for absorbent articles. In one respect, the inventions  
15 relates to a durably wettable, liquid pervious web which comprises:

- (i) an apertured web selected from the group consisting of polymeric films or nonwovens; and
- (ii) a substantially continuous hydrophilic coating, less than about 2.5 microns thick, on  
20 at least one surface of the web, wherein said hydrophilic coating is applied to the web by a remote plasma polymerization process;

wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle that is not more than about 60 degrees greater than the Pre Aging contact angle.

In a similar aspect respect, at least one surface of the treated web will have a Post Washing contact angle that is not more than about 60 degrees greater than the Pre Washing  
25 contact angle. Preferably, both conditions will exist in a single treated web.

The invention also relates to an absorbent article comprising a durably wettable, liquid pervious topsheet, the topsheet comprising a web and a hydrophilic coating on at least one surface of the web, wherein the hydrophilic coating is applied to the web by a remote plasma polymerization process. In other words, the topsheet of the article comprises the durably  
30 wettable, liquid pervious web of the present invention.

Finally, the invention relates to a remote plasma polymerization process for making the durably wettable, liquid pervious webs described herein.

## DETAILED DESCRIPTION OF THE INVENTION

### I. Durably Wettable, Liquid Pervious Webs

As discussed in detail below, the present invention relates to a durably wettable, liquid pervious web that is prepared by applying a hydrophilic coating to a starting polymeric film or nonwoven, using a radiation curing process.

As used herein, the term "web" refers to the starting substrate (i.e., a polymeric film or nonwoven) to which the hydrophilic coating is applied. In contrast, the terms "durably wettable, liquid pervious web" or "treated web" refer to the final product - the polymer film or nonwoven having the durable hydrophilic coating.

As used herein, the term "liquid pervious" refers to the ability of a web or treated web to transport liquids from one surface of the web or treated web to the opposite surface of the web or treated web in a sufficiently efficient manner so as to allow the treated web to be used as a component of a disposable article. Webs may be inherently liquid pervious or may be made liquid pervious by application of a processing step, such as, aperturing.

As used herein, the term "substantially continuous" means sufficiently continuous to provide the hydrophilic or wettable properties as defined by the stated or claimed contact angle limitations.

As used herein, the terms "hydrophilic" and "wetable" are used interchangeably and refer to surfaces that are wettable by aqueous liquids (e.g., aqueous body liquids) deposited on these surfaces. Hydrophilicity and wettability are typically defined in terms of contact angle and the surface tension of the liquids and solids involved. This is discussed in detail in the American Chemical Society publication entitled Contact Angle, Wettability and Adhesion, edited by Robert F. Gould (Copyright 1964). A web surface is said to be wetted by a liquid (i.e., hydrophilic) when either the contact angle between the liquid and the web surface is less than 90°, or when the liquid tends to spread spontaneously across the surface of the web, both conditions normally co-existing. Conversely, a surface is considered to be hydrophobic if the contact angle is greater than 90° and the liquid does not spread spontaneously across the surface of the web. In general, the lower the contact angle between the surface and the liquid, the more hydrophilic the surface.

The durably wettable, liquid pervious webs of the present invention are "durably wettable", insofar as the hydrophilic character engendered to the otherwise more hydrophobic film is maintained over time and after exposure to liquids. As discussed above, prior approaches directed at making hydrophobic films wettable result in initial improvements in wettability, but suffer from the negative attribute that wettability is lost over time and/or upon exposure to liquids. Durable wettability is described herein in terms of the ability of a durably wettable, liquid

pervious web (as indicated, referred to herein as a "treated web", to distinguish from the starting "web") to retain its wettable character after aging (referred to as "Post Aging") and/or after exposure to liquids (referred to as "Post Washing"). The methods for measuring Post Aging contact angle and Post Washing contact angle are discussed below.

5           As indicated, the durable wettability of the present polymeric webs is attained by use of a remote plasma process. While not being bound by theory, it is believed that typical hydrophilic polymer and surface-treated polymer systems, such as corona discharge treatments, go through a "hydrophobic recovery" process. During the hydrophobic recovery process, surface wettability tends to decay over time because thermodynamics favors the exposure of lower surface energy  
10       molecular chain segments at polymer surface. Upon aging, hydrophilic molecular segments reorient and embed themselves and expose hydrophobic segments at polymer surface. If chemical crosslinking is induced at the polymer surface, the crosslinking tends to limit polymer chain mobility, thus significantly slowing the "hydrophobic recovery" process and therefore preserving polymer surface wettability over time. Since Applicants' invention provides for  
15       polymer chemical crosslinking, via a remote plasma polymerization process, a durably wettable, liquid pervious web can be produced.

          As used herein, "remote plasma" and "after glow" each mean that monomer is injected outside of plasma zone or plasma glow and the substrate to be surface treated is placed outside of plasma glow, usually beneath the monomer injection opening. The benefit derived from  
20       placement outside the plasma zone is to avoid interaction of monomer molecules with the plasma electrons and ions which cause undesired monomer fragmentation. Since electrons and ions are short-lived species, they are confined inside the plasma glow. As used herein, "plasma zone" and "plasma glow" each refer to the portion of volume inside a chamber, normally in between the electrodes, which is significantly brighter than the remaining volume due to visible glow. The  
25       visible glow is produced by plasma excited species that undergo electronic relaxation accompanied by light emission.

          Plasma is often referred to as the fourth state of matter. When energy is applied to a solid (e.g., a polymeric film), the solid can undergo a transition to the liquid state. If further energy is applied, the liquid becomes a gas. If additional energy of the proper kind is applied, the gas  
30       dissociates and becomes plasma. For plasma polymerization to produce a coating on a web, which may also be called "plasma grafting", "plasma deposition" or "plasma coating", a suitable organic monomer or a mixture of monomers having polymerizable unsaturated groups is introduced into the plasma zone of the reactor where it is fragmented and/or activated forming further excited species in addition to the complex mixture of the activated plasma gases. The  
35       excited species and fragments of the monomer recombine upon contact with the web in an



undefined way to a largely undefined structure which contains a complex variety of different groups and chemical bonds forming a highly crosslinked polymer deposit on the web. If  $O_2$ ,  $N_2$  or oxygen- or nitrogen-containing molecules are present, either within the plasma reactor during the plasma coating process, or on exposure of the plasma coated substrate to oxygen or air subsequent to the plasma process, the polymeric deposit will include a variety of polar groups.

In one plasma technique, which is referred to herein as "in-glow" or "direct" plasma polymerization, the web to be treated and the monomers to be reacted are located within the plasma zone during the polymerization process. While this technique has been found useful for preparing durably wettable webs that are useful as topsheets for absorbent articles (see co-pending U.S. Patent Application Serial No. 09/157845, filed September 21, 1998 by Y. P. Lee et al. and titled DURABLY WETTABLE, LIQUID PERVIOUS POLYMERIC WEBS), polymerization within the plasma zone does have certain drawbacks. For instance, the monomers may become undesirably fragmented prior to deposition on the film. As such, the use of direct plasma polymerization limits to some degree the monomers that may be utilized. In contrast, the treated webs of the present invention are prepared using "remote" or "after-glow" (these terms are used interchangeably herein) plasma polymerization and therefore the concern of excess fragmentation is mitigated. Remote plasma polymerization is a process in which polymerization is effected in the presence of the plasma, but wherein the web as well as the inlet for the monomer feed are located outside of, or remote from (typically below), the plasma zone. Fragmentation of the monomer molecules can be largely avoided in this process, as the monomer does not pass the zone of the highly reactive plasma gases. As such, certain desirable monomers for forming the hydrophilic coating can be used in the present process, while they cannot be used where direct plasma polymerization is employed. With the present process, the structure of the polymer deposited can be controlled within certain limits, undesired surface erosion of susceptible substrates can be avoided and the formation of the polymer deposits is predominantly based on radical reactions.

Plasmas exist in a variety of forms. The plasma process useful herein is a remote, low pressure or vacuum process, which allows processing of the web at or near ambient temperature, i.e., about  $20^{\circ}C$ . This prevents thermal degradation of the web being processed and/or thermal distortion of the formed web that is being treated. Within the plasma chamber active species in the form of electrons, free-radicals, ions and energetic neutrals are formed and collide with the surface of the web, e.g. a polymer, (which is placed outside the plasma chamber) breaking molecular bonds and creating new functional groups on the web's surface. These active and energetic species also react in the gas phase, resulting in a thin coating being deposited on at least one surface of the web.

Suitable plasma systems for use in the present invention incorporate a parallel plate electrode design where materials to be treated are exposed to the primary field of RF energy, but are not part of the circuitry. With higher pressure processes (but still within the general definition of a cold gas plasma), some form of gas delivery system, designed to create a uniform laminar flow of process gas throughout the entire chamber volume is beneficial. In multiple electrode/shelf designs, it is important that each of the electrodes receive equal amounts of RF energy. In this manner a uniform glow discharge is created between each shelf or in each plasma zone. Solid state components and microprocessor control of the system parameters of process time, flow rate, power level, and working pressure, will also ensure process uniformity, efficiency, and repeatability.

Since plasmas are electrically conductive atmospheres, they carry a characteristic impedance to the output of the RF generator. Therefore, the preferred plasma process utilizes a matching network to constantly tune the plasma impedance to the output impedance of the RF generator. Advanced plasma systems suitable for use in the present invention are available from HIMONT Plasma Science, Foster City, Calif. (a business unit of HIMONT U.S.A., Inc.), and incorporate an automatic matching type of network and provisions for error checking during the process.


The low temperature plasma is generated in a gaseous atmosphere at reduced pressure of from about 0.001 to about 10 Torr, preferably from about 0.01 to about 5 Torr, more preferably from about 0.05 to about 1 Torr, and most preferably from about 0.05 to about 0.4 Torr. The electric power can be supplied to the equipment at a high radio frequency, from about 40 KHz to 3 GHz, preferably from 13 to 27 MHz, and most conveniently at about 14 MHz. To achieve the desired plasma condition in the gaseous atmosphere, the electric power delivered to the apparatus can vary over a range of from about 1 to about 10,600 watts; preferably from about 10 to about 1,000 watts, more preferably from about 50 to about 500 watts, most preferably from about 75 to about 250 watts. The power used is somewhat dependent on the chamber's working volume. The most preferred 75 to 250 watts is appropriate for HIMONT Plasma Science PS0500D gas plasma apparatus with a working volume of 5.0 cubic feet. The plasma treatment time varies from a few seconds to several minutes, preferably from about 20 seconds to about 30 minutes, most preferably from 60 seconds to about 20 minutes.

It should be appreciated that treatment pressure, time and power are interrelated, rather than independent, variables. The effect of the level selected for each of these variables will determine the extent of web surface modification and/or coating thickness; also related are the chamber volume and geometry as well as the sample size and surface geometry. The selection of the level for these variables is well within the ordinary skill of practitioners in the art to which this

invention pertains.

The hydrophilic coating layer is deposited onto the surface of a suitable web (either previously apertured or unapertured) via remote plasma-induced vapor deposition (i.e., polymerization) of a monomer or combination of monomers, such that a hydrophilic coating will be applied to the web. The monomer(s) which may be used to prepare the polymeric coatings by after-glow plasma-induced polymerization may be any polymerizable unsaturated compound which can be evaporated and introduced into the after-glow zone of a plasma generating apparatus to contact the web provided therein. Preferred monomers are vinyl compounds, including but not limited to:

- a) acrylic and methacrylic acid of the general formula  $H_2C=C(R^2)-C(O)OH$ ,
- b) acrylates and methacrylates of the general formula  $H_2C=C(R^2)-C(O)OR^3$ ,
- c) acrylamides and methacrylamides of the general formula  $(R^2)(R^2)C=C(R^2)-C(O)NHR^3$ ,
- d) maleic and fumaric acid of the general formula  $HO(O)C-C(R^2)=C(R^2)-C(O)OH$ ,
- e) maleates and fumarates of the general formula  $R^3O(O)C-C(R^2)=C(R^2)C(O)OR^3$ ,
- f) vinyl ethers of the general formula  $(R^2)(R^2)C=C(R^2)-O-R^3$ ,
- g) N-vinyl-2-pyrrolidone of the formula  $(R^2)(R^2)C=C(R^2)-N-CH_2-CH_2-CH_2-C(O)$ ,  


- h) vinyl acetate of the general formula  $(R^2)(R^2)C=C(R^2)-OC(O)CH_3$ , and
- i) aliphatic vinyl compounds of the general formula  $R^2CH=CHR^3$ , and mixtures thereof,

where each  $R^2$  is independently hydrogen or  $C_1$ - $C_{10}$  alkyl, preferably  $C_1$ - $C_5$  alkyl, and each  $R^3$  is independently an aliphatic hydrocarbon group of up to about 10 carbon atoms which is unsubstituted or is substituted by one or more polar groups such as carboxy, hydroxy, amino, and a (poly)ethylene oxide group or substituted by one or more sulfate, phosphate, sulfonate groups or mixtures of such groups.

Specific examples of preferred acrylic derivatives include acrylic acid, methacrylic acid, hydroxyethylmethacrylate (HEMA), methylmethacrylate (MMA), dimethylaminoethylmethacrylate (DMAEMA), 2-hydroxyethylacrylate (HEA), N,N-dimethylacrylamide (DMA), N-acryloylmorpholine (NAM) and ethylene glycol dimethacrylate (EGDMA). Specific examples of suitable vinyl ethers are methylvinyl ethers, ethylvinyl ether and methoxyethylvinyl ether. Suitable hydrophilic monomers also include ethylene glycol, ethylene oxide and propylene oxide. The monomers can be used individually or as mixtures of monomers.

Prior to being introduced into the chamber, the monomer is heated to a temperature sufficient to vaporize the compound and to create sufficient vapor pressure such that the coating is deposited at a reasonable speed. Typically, the temperature will be from about 40° to about

100°C, more typically from about 40° to about 60°C. Oxygen in gaseous form and argon is optionally fed into the deposition chamber simultaneously with, but each with a separate feeding means and mass flow controller, the gaseous monomer compound. Depending upon the application, the O<sub>2</sub> flow rate ranges from 5 standard cubic centimeter/minute ("sccm") to 1200 sccm, the gaseous monomer compound flow is from 1 sccm to 250 sccm, and Ar flow is from 1 sccm to 150 sccm. Argon is used to enhance the rate of deposition of the gaseous materials being employed and, therefore, it is preferable to use Argon in the process.

Alternatively, monomer deposition may be achieved via the flash vaporization technique that is described in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

The low temperature plasma is generated in a gaseous atmosphere at reduced pressure of from about 0.001 to about 10 Torr, preferably from about 0.01 to about 5 Torr, more preferably from about 0.05 to about 1 Torr, and most preferably from about 0.05 to about 0.4 Torr, depending on the process used and the web being treated.

With respect to the starting web, the web may be flat (two dimensional) or complex (three dimensional, including previously apertured films) prior to plasma deposition of the hydrophilic coating. That is, plasma polymerization may be conducted either before or after formation of the apertures of the web. In a preferred embodiment, plasma treatment will be conducted after aperture formation, so as to better preserve a uniform hydrophilic coating on the film's surface.

The aforementioned advanced plasma systems available from HIMONT Plasma Science, such as the PS0500D reactor are equipped with a throttle valve, thereby making it possible to achieve a range of process pressures with the same gas flow rate.

The plasma treatment time for obtaining the desired hydrophilic coatings is from about 0.1 minute to about 10 minutes, preferably from about 1.5 to about 4 minutes, most preferably from about 1.5 to about 2.5 minutes; and the RF power used to cause reaction of the vapor is preferably from about 10 to about 1,000 watts, more preferably from about 50 to about 500 watts, most preferably from about 75 to about 250 watts. The RF power employed ranges from about 100 to about 2500 watts and depends on the substrate being treated and the throughput requirements. The resulting hydrophilic coatings can be produced in different thicknesses, but typically is from about 0.01 to about 2.5 microns, preferably from about 0.5 to about 1 microns.

While performing the remote plasma polymerization, the web is preferably positioned at a distance of from about 1 to about 40 cm below the plasma zone. Similarly, the monomer inlet is preferably positioned at a distance of from about 1 to about 35 cm below the plasma zone. The web distance downstream from (i.e., below) the plasma zone is more preferably from about 2 to about 20 cm, and most preferably from about 3 to about 10 cm. The monomer inlet distance

downstream from the plasma zone is preferably from about 2 to about 20 cm, and most preferably from about 3 to about 10 cm.

In one preferred embodiment, remote plasma polymerization of a polymerizable unsaturated compound in accordance with the invention is preferably carried out under the following plasma conditions:

5	Electric power	10-100 watts
	Electric voltage	$8 \cdot 10^2$ - $4 \cdot 10^3$ volts
	Plasma gas flow	1 -100 sccm (standard cubic centimeter)
	Monomer flow	1-50 mg/min
10	Feed gas flow	1-100 sccm
	Temperature of the monomer source	-80°C - +80°C
	Frequency	1 kHz - 27.12 MHz, most preferably 13.6 or 27.12 MHz
	Plasma gases	Ar, He, N <sub>2</sub>
15	Pressure	0.01-1 torr

The polymeric coatings of the present invention which are obtainable by remote plasma-induced polymerization of a polymerizable unsaturated compound on a web under the aforementioned conditions regarding the distance between web and plasma zone, as well as monomer inlet and plasma zone, are characterized - contrary to coatings obtained by in-glow (or direct) plasma-induced polymerization - by the fact that the repeating units of the polymer chains are to a large extent identical in structure to those repeating units obtained through a non-plasma radical polymerization of the respective unsaturated compound. Typically from about 70% to about 98%, more typically from about 76% to about 98% and most typically from about 82% to about 98% of the repeating structural units exhibit the same structure as the polymer obtained by non-plasma radical polymerization of the same monomer. Typically, from about 2% to about 30%, more typically from about 2% to about 24%, still more typically from about 2% to about 18% of the remaining structural units serve as covalent linking groups to the treated web or as crosslinking sites between adjacent polymer chains.

The qualitative and quantitative characterization of a plasma-induced polymer coating of the present invention may typically be determined as outlined below.

The uniform structure and the controllable relatively low degree of crosslinking of the coatings which is surprisingly achieved using remote plasma polymerization of a polymerizable unsaturated compound under the specific conditions of the position of substrate and monomer inlet constitutes a characteristic feature of the coatings which is responsible for the durable

wettability of the treated webs. A specific advantage of the coatings is their strong adherence to the surface of the treated web which is obtained to a large degree independently from the nature of the web.

As indicated, the plasma induced hydrophilic coating exhibits a contact angle for water of  
5 less than about 90 degree, such that any water or aqueous-based liquid placed on the web will tend to spread spontaneously over the web's coated surface. In a preferred embodiment, the treated web may be further treated by exposure to a low temperature plasma gas composition (also referred to herein as a "surface modifying gas stream") or an energy source (also referred herein as "radiation curing") such as an apparatus that emits, including but not limited to, infra  
10 red, electron beam, thermionic or ultra violet radiation. Apparatuses that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein.

In the surface modifying gas stream embodiment the gas stream preferably comprises  $N_2O$  and  $CO_2$ , to enhance the durability of the hydrophilic coating. In one such preferred  
15 embodiment, the plasma gas composition will comprise from about 80 to about 40 mol %  $N_2O$  and from about 20 to about 60 mol %  $CO_2$ , preferably from about 70 to about 45 mol %  $N_2O$  and from about 30 to about 55 mol %  $CO_2$ , most preferably from about 60 to about 45 mol %  $N_2O$  and from about 40 to about 55 mol %  $CO_2$ , where the amount of  $N_2O$  and  $CO_2$  in the mixture equals 100 to 10 mol %, for a time sufficient to modify the surface of the hydrophilic coating to enhance  
20 its durability.

In the radiation curing embodiment, the radiation source is preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter window onto the monomer, thereby further curing the monomer, which enhances the durability of the hydrophilic coating. Curing is controlled by matching the electron beam voltage to the dielectric thickness of  
25 the monomer coating. For example, a 10 Kv electron voltage will penetrate about 1 micron of deposited monomer.

The plasma process is generally practiced as follows. The web to be treated is placed into a vacuum chamber and the chamber pressure is reduced, typically to about 0.005 Torr. The process gas or gas mixture employed is introduced to the chamber and the chamber pressure is  
30 stabilized at a pressure of 0.04-0.4 Torr. The interior dimension of the work area is approximately 1.73 X 0.76 X 1.02 meters (width x height x depth) for a total working volume of 1.34 cubic meters. A suitable high frequency form of energy, typically 13.56 MHz radio frequency energy, is used to create the plasma; in the system described, this is achieved with a total power input capacity of up to 2500 watts. The RF energy dissociates the gas, creating a  
35 plasma characterized by a distinctive glow. Since the process is conducted at reduced pressures,

the bulk temperature of the gas is near ambient temperature, thus the reference to a cold gas plasma, a glow discharge, or a cold gas glow discharge. The electrons or ions created in the plasma bombard the web's surface, abstracting atoms or breaking bonds, creating free radicals. These free radicals are unstable and seek to satisfy a more stable state by reacting with free radicals or groups within the plasma gas, also establishing new moieties on the surface of the web. In addition, the energetic electrons in the glow discharge fragment the molecules in the gas phase, leading to complex chemical reactions that result in a thin hydrophilic coating being deposited on at least one surface of the web.

Typically, and preferably, before plasma deposition of the hydrophilic coating, an initial step is performed. The purpose of this step is to clean the web surface to be treated to promote adhesion of the subsequently deposited thin hydrophilic coating. Cleaning may be accomplished by subjecting the web's surface to radiation (herein referred to as radiation cleaning) from an energy source including but not limited to, infra red, electron beam, thermionic and ultra violet radiation or by plasma cleaning. Apparatuses that are suitable as energy sources in the present invention are disclosed in U.S. Patent No. 4,842,893 issued to Yializis on Apr. 29, 1988, the disclosure of which is incorporated by reference herein. In the radiation cleaning embodiment, the radiation source is preferably a gas discharge electron beam gun. The gun directs a flow of electrons through a emitter window onto the web's surface, thereby abstracting atoms or breaking bonds, thus creating free radicals. These free radicals are unstable and seek to satisfy a more stable state thus they serve as bonding sites for the monomers that are used to produce the web's hydrophilic coating. Cleaning is controlled by matching the electron beam voltage to the dielectric thickness or depth of cleaning that is desired. For example, a 10 Kv electron voltage will penetrate to a film depth of about 1 micron.

In the plasma cleaning embodiment, the gases are typically either Ar alone, O<sub>2</sub> alone, or mixtures (e.g., 1:1) of Ar and O<sub>2</sub>. Gas flow rates are typically in the range of 20-100 sccm (standard cc/min), preferably 40-80 sccm, and most preferably 50-60 sccm. RF power is approximately 1100 watts, and process pressure is about 0.04 Torr. After the optional initial step, the next step is the plasma deposition of the hydrophilic coating, as described above and in more detail in the examples below.

The materials useful as polymeric films to be plasma treated to provide a hydrophilic coating will be derived from thermoplastic polymers. In general, the term "thermoplastic polymer" is used herein to mean any thermoplastic polymer which can be used for the preparation of films. Examples of thermoplastic polymers include, by way of illustration only, end-capped polyacetals, such as poly(oxymethylene) or polyformaldehyde, poly(trichloroacetaldehyde), poly(n-valeraldehyde), poly(acetaldehyde), poly(propionaldehyde), and the like; acrylic

polymers, such as polyacrylamide, poly(acrylic acid), poly(methacrylic acid), poly(ethyl acrylate), poly(methyl methacrylate), and the like; fluorocarbon polymers, such as poly(tetrafluoroethylene), perfluorinated ethylene-propylene copolymers, ethylene-tetrafluoroethylene copolymers, poly(chlorotrifluoroethylene), ethylene-chlorotrifluoroethylene copolymers, poly(vinylidene fluoride), poly(vinyl fluoride), and the like; polyamides, such as  
5 poly(6-aminocaproic acid) or poly( $\epsilon$ -caprolactam), poly(hexamethylene adipamide), poly(hexamethylene sebacamide), poly(11-aminoundecanoic acid), and the like; polyaramides, such as poly(imino-1,3-phenyleneiminoisophthaloyl) or poly(m-phenylene isophthalamide), and the like; polyarylenes, such as poly-p-xylylene, poly(chloro-p-xylylene), and the like; polyaryl  
10 ethers, such as poly(oxy-2,6-dimethyl-1,4-phenylene) or poly(p-phenylene oxide), and the like; polyaryl sulfones, such as poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenylene-isopropylidene-1,4-phenylene), poly-(sulfonyl-1,4-phenyleneoxy-1,4-phenylene-sulfonyl-4,4'-biphenylene), and the like; polycarbonates, such as poly(bisphenol A) or poly(carbonyldioxy-1,4-phenylene-isopropylidene-1,4-phenylene), and the like; polyesters, such as poly(ethylene  
15 terephthalate), poly(tetramethylene terephthalate), poly(cyclohexylene-1,4-dimethylene terephthalate) or poly(oxymethylene-1,4-cyclohexyl-enemethyleneoxyterephthaloyl), and the like; polyaryl sulfides, such as poly(p-phenylene sulfide) or poly(thio-1,4-phenylene), and the like; polyimides, such as poly(pyromellitimido-1,4-phenylene), and the like; polyolefins, such as polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene),  
20 poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, polychloroprene, polyacrylonitrile, poly(vinyl acetate), poly(vinylidene chloride), polystyrene, and the like; copolymers of the foregoing, such as acrylonitrile-butadiene-styrene (ABS) copolymers, and the like.

Preferred polymers are polyolefins and polyesters, with polyolefins being more preferred.  
25 Even more preferred are those polyolefins which contain only hydrogen and carbon atoms and which are prepared by the addition polymerization of one or more unsaturated monomers. Examples of such polyolefins include, among others, polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, and the like. In  
30 addition, such term is meant to include blends of two or more polyolefins and random and block copolymers prepared from two or more different unsaturated monomers. Because of their commercial importance, the most preferred polyolefins are polyethylene and polypropylene.

In addition to polymeric films, webs that can be used to produce the durably wettable, liquid pervious webs of the present invention include but are not limited to spun bonded,  
35 hydroentangled, needled and polymerically bound nonwovens. Suitable nonwoven webs are



typically formed from organic textile fibers including but not limited to cotton, wool, wood, jute, viscous rayon, nylon, polyester, polyolefins, carbon, or mixtures thereof. Inorganic fibers such as glass and metal can be used alone or in combination or further combined with organic fibers. In the case of staple fibers, fiber length varies from about 1/4 inch to about 2 or more inches. In the case of spun bonded webs, the fiber lengths are indefinite. The staple fibers used in hydroentangled, needled and polymericly bound nonwovens are processed through conventional textile machinery.

For example, in producing a polymericly bound nonwoven web, a carding machine may be used to form a continuous length of rather two-dimensional loosely associated fibers known as a carded web. These webs may be assembled to form a multiple layer or three-dimensional fibrous web of significant weight, e.g., from about several grams to thousands of grams per yard. In continuous nonwoven fibrous webs, the textile fibers are arrayed at various angles to the lengthwise axis of the web. When a web is formed by the action of a carding machine, the fibers are usually predominantly oriented in the machine direction and, on the other hand, isotropic webs may be formed such as by air-laying. The fibrous webs described above are typically impregnated with a polymeric binding agent (polymericly bound). In a preferred form, the polymeric binders are applied as emulsions of acrylic, polyvinylacetate, or similar polymeric nature, and mixtures thereof. Preferably, the fibers are unwoven and substantially haphazardly oriented and adhesively bonded together with polymeric binder.

Hydroentangled and needled webs are distinct from polymericly bound webs as they rely principally on the physical entanglement of their fibers to provide web integrity. In contrast to polymericly bound and physically entangled webs, spun bond webs typically are composed of fibers of infinite length that are bound together through solvent or melt processes.

As indicated, the webs may be two-dimensional or may have an apertured three dimensional structure made in accordance with the teachings of the incorporated references discussed in the Background section, *supra*. The coatings are durable and increase the surface energy of the to render the resulting treated web more wettable. The coating is durable, in that it is maintained over time, even after exposure to water or other aqueous liquids. In this regard, the webs of the present invention are described in one respect in terms of their ability to remain wettable over time and/or after exposure to liquids. The ability to remain wettable over time is assessed by measuring the treated web's Post Aging contact angle. This measurement involves storing the plasma treated web at 74° C for 16 hours, to artificially age the sample, before measuring contact angle. The ability to remain wettable after exposure to liquids is assessed by measuring the treated web's Post Washing contact angle. This measurement involves placing a 2

in. x 2 in. sample of treated web in a 250 ml water bath at 65° C for 90 sec with vigorous agitation prior to measuring contact angle. Procedures and devices for measuring contact angle between a liquid and a web surface are well known in the art. However, the treated web that Applicants' have disclosed is tested for surface water drop contact angle and surface energy according to the procedures specified by T565 pm-96 provisional method and ACCU DYNE TEST, Diversified Enterprises (based on ASTM D2578-84 technique). Contact angle values are reported as the average of measurements on 5 samples.

In one aspect, the treated web of the present invention will have a Post Aging contact angle that is not more than about 60 degrees greater than the treated web's Pre Aging contact angle (i.e., the contact angle as measured before storage at 74°C for 16 hours). Preferably, the treated web will have a Post Aging contact angle that is not more than about 40 degrees, more preferably not more than about 20 degrees, still more preferably not more than about 10 degrees, greater than the Pre Aging contact angle. In another respect, the treated web of the present invention will have a Post Washing contact angle that is not more than about 60 degrees greater than the treated web's Pre Washing contact angle (i.e., the contact angle as measured before the treated web is placed in a 250 ml water bath at 65° C for 90 sec with vigorous agitation). In this regard, the treated web will preferably have a Post Washing contact angle that is not more than about 40 degrees, more preferably not more than about 20 degrees, still more preferably not more than about 10 degrees, greater than the Pre Washing contact angle. In a preferred aspect, the treated web of the present invention will exhibit both the Post Aging and Post Washing requirements discussed above.

The durably wettable, liquid pervious webs of the present invention will exhibit either (preferably both) a Post Aging or a Post Washing contact angle of less than about 90 degrees, preferably not more than about 70 degrees, more preferably not more than about 50 degrees, still more preferably not more than about 30 degrees, and most preferably not more than about 20 degrees.

## II. Absorbent Articles

As used herein, the term "absorbent article" refers generally to devices used to absorb and contain body exudates, and more specifically refers to devices which are placed against or in proximity to the body of the wearer to absorb and contain the various exudates discharged from the body. The term "absorbent article" is intended to include diapers, catamenial pads, tampons, sanitary napkins, incontinent pads, training pants and the like, as well as wipes, bandages and wound dressings. The term "disposable" is used herein to describe absorbent articles which are

not intended to be laundered or otherwise restored or reused as an absorbent article (i.e., they are intended to be discarded after limited use, and, preferably, to be recycled, composted or otherwise disposed of in an environmentally compatible manner). A "unitary" absorbent article refers to absorbent articles which are formed as a single structure or as separate parts united together to  
5 form a coordinated entity so that they do not require separate manipulative parts such as a separate holder and pad.

It is to be understood that the overall size, shape, and/or configuration of the absorbent article, if any, into which the durably wettable, liquid pervious webs of the present invention are incorporated, or utilized in conjunction with, have no criticality or functional relationship to the  
10 principles of the present invention. Such parameters, however, must be considered along with the intended liquid and intended functionality when determining appropriate web configurations.

In addition to the durably wettable, liquid pervious webs of the present invention, absorbent articles will also comprise an absorbent core for retention of any absorbed body liquids. Exemplary absorbent structures for use as the absorbent core in the present invention are  
15 described in U.S. Patent No. 4,950,264 issued to Osborn on August 21, 1990; U.S. Patent No. 4,610,678 issued to Weisman et al. on September 9, 1986; U.S. Patent No. 4,834,735 issued to Alemany et al. on May 30, 1989; European Patent Application No. 0 198 683, the Procter & Gamble Company, published October 22, 1986 in the name of Duenk et al.; U.S. Patent No. 4,673,402 issued to Weisman et al. on June 16, 1987; and U.S. Patent No. 4,888,231 issued to  
20 Angstadt on December 19, 1989. The absorbent core may further comprise the dual core system containing an acquisition/distribution core of chemically stiffened fibers positioned over an absorbent storage core as detailed in U.S. Patent No. 5,234,423, entitled "Absorbent Article With Elastic Waist Feature and Enhanced Absorbency" issued to Alemany et al., on August 10, 1993; and in U.S. Patent No. 5,147,345, entitled "High Efficiency Absorbent Articles For Incontinence  
25 Management" issued to Young, LaVon and Taylor on September 15, 1992. The disclosure of all of these patents is incorporated herein by reference.

A preferred embodiment of a unitary disposable absorbent article made in accordance herewith is a catamenial pad, or sanitary napkin. As used herein, the term "sanitary napkin" refers to an absorbent article which is worn by females adjacent to the pudendal region, generally  
30 external to the urogenital region, and which is intended to absorb and contain menstrual liquids and other vaginal discharges from the wearer's body (e.g., blood, menses, and urine). Interlabial devices which reside partially within and partially external to the wearer's vestibule are also within the scope of this invention. Suitable feminine hygiene articles are disclosed in U.S. Patent No. 4,556,146, issued to Swanson et al. on Dec. 3, 1985, U.S. Patent No. 4,589,876, issued to  
35 Van Tilberg on April 27, 1993, U.S. Patent No. 4,687,478, issued to Van Tilburg on Aug. 18,

1987, U.S. Patent No. 4,950,264, issued to Osborn, III on Aug. 21, 1990, U.S. Patent No. 5,009,653, issued to Osborn, III on April 23, 1991, U.S. Patent No. 5,267,992, issued to Van Tilburg on Dec. 7, 1993, U.S. Patent No. 5,389,094, issued to Lavash et al. on Feb. 14, 1995, U.S. Patent No. 5,413,568, issued to Roach et al. on May 9, 1995, U.S. Patent No. 5,460,623, issued to  
5 Emenaker et al. on Oct. 24, 1995, U.S. Patent No. 5,489,283, issued Van Tilburg on Feb. 6, 1996, U.S. Patent No. 5,569,231, issued to Emenaker et al. on Oct. 29, 1996, and U.S. Patent No. 5,620,430, issued to Bamber on April 15, 1997, the disclosure of each of which is incorporated by reference herein.

In a preferred embodiment of the present invention, the sanitary napkin has two flaps  
10 each of which are adjacent to and extend laterally from the side edge of the absorbent core. The flaps are configured to drape over the edges of the wearer's panties in the crotch region so that the flaps are disposed between the edges of the wearer's panties and the thighs. The flaps serve at least two purposes. First, the flaps help serve to prevent soiling of the wearer's body and panties by menstrual liquid, preferably by forming a double wall barrier along the edges of the panty.  
15 Second, the flaps are preferably provided with attachment means on their garment surface so that the flaps can be folded back under the panty and attached to the garment facing side of the panty. In this way, the flaps serve to keep the sanitary napkin properly positioned in the panty. The flaps can be constructed of various materials including materials similar to the topsheet, backsheet, tissue, or combination of these materials. Further, the flaps may be a separate element attached to  
20 the main body of the napkin or can comprise extensions of the topsheet and backsheet (i.e., unitary). A number of sanitary napkins having flaps suitable or adaptable for use with the sanitary napkins of the present invention are disclosed in U.S. Patent No. 4,687,478 entitled "Shaped Sanitary Napkin With Flaps", which issued to Van Tilburg on August 18, 1987; and U.S. Patent No. 4,589,876 entitled "Sanitary Napkin", which issued to Van Tilburg on May 20, 1986.  
25 The disclosure of each of these patents is hereby incorporated herein by reference.

In a preferred embodiment of the present invention, an acquisition layer(s) may be positioned between the topsheet and the absorbent core. The acquisition layer may serve several functions including improving wicking of exudates over and into the absorbent core. There are several reasons why the improved wicking of exudates is important, including providing a more  
30 even distribution of the exudates throughout the absorbent core and allowing the sanitary napkin to be made relatively thin. The wicking referred to herein may encompass the transportation of liquids in one, two or all directions (i.e., in the x-y plane and/or in the z-direction). The acquisition layer may be comprised of several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene; natural fibers  
35 including cotton or cellulose; blends of such fibers; or any equivalent materials or combinations

of materials. Examples of sanitary napkins having an acquisition layer and a topsheet are more fully described in U.S. Patent No. 4,950,264 issued to Osborn and U.S. Patent Application Serial No. 07/810,774, "Absorbent Article Having Fused Layers", filed December 17, 1991 in the names of Cree, et al. The disclosures of each of these references are hereby incorporated herein by  
5 reference. In a preferred embodiment, the acquisition layer may be joined with the topsheet by any of the conventional means for joining webs together, most preferably by fusion bonds as is more fully described in the referenced Cree application.

Catamenial pads may be constructed as follows. Onto silicone-coated release paper a spiral pattern of H2031 Findlay hot melt adhesive is applied at 0.04 g/in<sup>2</sup>. This adhesive layer is  
10 transferred onto the top (wearer-facing) side of a secondary topsheet by rolling the secondary topsheet and coated release paper together with a hand roller. The secondary topsheet is formed of a nonwoven material known as Fort James Airlaid Tissue, Grade 817, commercially available from the Fort James Corp. of Green Bay, Wisconsin. A topsheet of the present invention is applied to the adhesive side of the secondary topsheet and the two are bonded by gently pressing  
15 them together with a hand roller. Two strips of one-quarter-inch double-sided tape are applied along both long edges of a polyethylene backsheet. The absorbent core is added to construct the complete absorbent structure.

As used herein, the term "diaper" refers to a garment generally worn by infants and incontinent persons that is worn about the lower torso of the wearer. It should be understood,  
20 however, that the present invention is also applicable to other absorbent articles such as incontinent briefs, incontinent pads, training pants, diaper inserts, facial tissues, paper towels, and the like. In general, a diaper of the present invention will comprise a topsheet comprising the durably wettable, liquid pervious web of the present invention; a liquid impervious backsheet joined with the topsheet; and an absorbent core positioned between the topsheet and the  
25 backsheet. Additional structural features such as elastic members and fastening means for securing the diaper in place upon a wearer (such as tape tab fasteners) may also be included.

While the topsheet, the backsheet, and the absorbent core can be assembled in a variety of well known configurations, a preferred diaper configuration is described generally in U.S. Patent No. 3,860,003 (Buell), issued January 14, 1975, the disclosure of which is incorporated by  
30 reference. Alternatively, preferred configurations for disposable diapers herein are also disclosed in U.S. Patent No. 4,808,178 (Aziz et al.), issued February 28, 1989; U.S. Patent No. 4,695,278 (Lawson), issued September 22, 1987; and U.S. Patent No. 4,816,025 (Foreman), issued March 28, 1989, the disclosures of each of these patents hereby being incorporated herein by reference. Suitable incontinence articles for adult wearers are disclosed in U.S. Patent No. 4,253,461 issued  
35 to Strickland, et al. on March 3, 1981; U.S. Patent Nos. 4,597,760 and 4,597,761 issued to Buell;

U.S. Patent No. 4,704,115; U.S. Patent No. 4,909,802 issued to Ahr, et al.; U.S. Patent No. 4,964,860 issued to Gipson, et al. on October 23, 1990; and in U.S. Patent Application Serial No. 07/637,090 filed by Noel, et al. on January 3, 1991 (PCT Publication No. WO 92/11830 published on July 23, 1992). The disclosure of each of these references is incorporated herein.

5       The absorbent core of the diaper is positioned between the topsheet and the backsheet. The absorbent core can be manufactured in a wide variety of sizes and shapes (e.g., rectangular, hourglass, asymmetrical, etc.). The total absorbent capacity of the absorbent core should, however, be compatible with the design liquid loading for the intended use of the absorbent article or diaper. Further, the size and absorbent capacity of the absorbent core can vary to  
10       accommodate wearers ranging from infants through adults.

As indicated, the absorbent core may include a liquid distribution member. In a preferred configuration, the absorbent core preferably further includes an acquisition layer or member in liquid communication with the liquid distribution member and located between the liquid distribution member and the topsheet. The acquisition layer or member may be comprised of  
15       several different materials including nonwoven or woven webs of synthetic fibers including polyester, polypropylene, or polyethylene, natural fibers including cotton or cellulose, blends of such fibers, or any equivalent materials or combinations of materials.

In a preferred embodiment, the diaper will comprise elasticized leg cuffs. The elasticized leg cuffs can be constructed in a number of different configurations, including those described in  
20       U.S. Patent No. 3,860,003; U.S. Patent No. 4,909,803, issued to Aziz et al. on Mar. 20, 1990; U.S. Patent No. 4,695,278, issued to Lawson on Sep. 22, 1987; and U.S. Patent No. 4,795,454, issued to Dragoo on Jan. 3, 1989, each being incorporated herein by reference.

In use, the diaper is applied to a wearer by positioning the back waistband region under the wearer's back, and drawing the remainder of the diaper between the wearer's legs so that the  
25       front waistband region is positioned across the front of the wearer. The tape-tab or other fasteners are then secured preferably to outwardly facing areas of the diaper.

### III. Examples

The following examples are illustrative and are not meant as a limitation of the invention  
30       disclosed and claimed herein.

#### Example 1

A test web of polyethylene film material (30 cm x 20 cm) is placed on the bottom (20 cm

below the bottom electrode) of a vacuum chamber of plasma discharge unit (APS Inc. Model D). The plasma chamber is evacuated. When the pressure inside the chamber reaches 20 mTorr, a carrier gas (Ar) is continuously introduced into the chamber at a constant rate (10 sccm), so the pressure inside the chamber is maintained at 63 mTorr by the balance of continuous evacuation and introduction of carrier gas. While keeping the conditions described above, low temperature plasma is generated inside the chamber for a period of 1 min. by supplying a high frequency electric power of 100 W at a frequency 40 kHz to expose the surface of the film to the low temperature plasma. Then, a monomer (acrylic acid) is introduced into the chamber at a constant rate to maintain constant pressure in the chamber (165 mTorr). While maintaining the conditions described above, low temperature plasma (100 W, 40 kHz) is generated inside the chamber for a period of 10 min. After the treatment, the chamber is evacuated (30 mTorr) and flooded with atmospheric air. The treated web is tested for surface water drop contact angle and surface energy according to the procedures specified by T565 pm-96 provisional method and ACCU DYNE TEST, Diversified Enterprises (based on ASTM D2578-84 technique), to give the results shown in Table 1.

Table 1

Example	fresh sample surface energy (dyne/cm)	fresh sample contact angle (deg)	aged sample <sup>a</sup> surface energy (dyne/cm)	aged sample <sup>a</sup> contact angle (deg)
1	>60	10	>60	10

<sup>a</sup>: samples where kept in an oven at 74°C for 16 hrs before contact angle measurement.

#### Comparative Examples 2-4

This example presents the contact angle data (as shown in Table 2, to be compared with Table 1) for a polyethylene film exposed to a carrier gas (Ar) and a monomer (acrylic acid) without plasma discharge (Example 2), a film exposed to a carrier gas (Ar) and plasma discharge (100 W) for 11 min (Example 3), and a film placed in between the electrodes (direct plasma) exposed to a carrier gas (Ar), a monomer (acrylic acid), and plasma discharge (100 W, 11 min) (Example 4). From comparison with Table 1, it is seen that remote plasma provides a web that better retains its hydrophilicity after accelerated aging, relative to a web prepare under various other conditions, including direct plasma polymerization.

Table 2

Examples	fresh sample surface energy	fresh sample contact angle <sup>a</sup>	aged sample surface energy	aged sample contact angle <sup>a</sup>
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	dyne/cm	deg.	dyne/cm	deg.
2	30	100	30	101
3	>60	15	54	57
4	>60	40	56	53

<sup>a</sup>: contact angle value is an average of 5 measurements



What is claimed is:

1. A remote plasma process for making a durably wettable, liquid pervious web for use as a topsheet in an absorbent article, the process comprising:

- (i) introducing a web to a plasma reaction chamber comprising a plasma reaction zone, wherein the web is placed outside the plasma reaction zone; and
- (ii) coating at least one of the surfaces of the web with polymerized monomers by plasma polymerization, wherein the coating is less than 2.5 microns thick and is derived from a monomer gas stream that will provide a hydrophilic coating upon plasma polymerization and wherein the monomer gas stream is introduced outside the plasma reaction zone;

said process characterized in that the web is selected from the group consisting of polymeric films, apertured polymeric films, nonwovens and apertured nonwovens; wherein the polymerized monomers cause at least one surface of the web to become durably-wettable.


2. The process of Claim 1 wherein at least one surface of the durably-wettable, liquid pervious web has a Post Aging contact angle that is not more than 60 degrees greater than the Pre Aging contact angle, preferably not more than 40 degrees greater than the Pre Aging contact angle and most preferably not more than 20 degrees greater than the Pre Aging contact angle.

3. The process of any preceding claim wherein at least one surface of the durably-wettable, liquid pervious web has a Post Washing contact angle that is not more than 60 degrees greater than the Pre Washing contact angle, preferably is not more than 40 degrees greater than the Pre Washing contact angle and most preferably not more than 20 degrees greater than the Pre Washing contact angle.

4. The process of any preceding claim wherein the process further comprises the step of cleaning the surface of the web by exposing the surface to plasma conditions or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof, prior to introduction of the monomer gas stream of step (ii).

5. The process of Claim 4 wherein the step of cleaning the surface of the web by exposing the web to plasma conditions comprises introduction of a gas stream comprising a material selected from the group consisting of Ar, O<sub>2</sub>, and mixtures thereof.

6. The process of any preceding claim wherein the process comprises the step of further modifying the hydrophilic surface by introducing the web formed in step (ii) to a surface modifying gas stream, the gas stream comprising  $N_2O$  and  $CO_2$ ; or an energy source or an energy source selected from the group consisting of infra red, electron beam, thermionic or ultra violet radiation and mixtures thereof.
7. The process of any preceding claim further comprising a final step comprising aperturing the coated web.
8. The process of any preceding claim wherein the polymeric film is derived from a material selected from the group consisting of polyolefins, polyesters, and mixtures thereof.
9. The process of Claim 8 wherein the polymeric film is derived from a material selected from the group consisting of polyethylene, polypropylene, poly(1-butene), poly(2-butene), poly(1-pentene), poly(2-pentene), poly(3-methyl-1-pentene), poly(4-methyl-1-pentene), 1,2-poly-1,3-butadiene, 1,4-poly-1,3-butadiene, polyisoprene, blends thereof, random copolymers thereof, and block copolymers thereof.
10. The process of any preceding claim wherein the monomer gas stream comprises a monomer containing at least one vinyl group.
11. The process of Claim 10 wherein the monomer gas stream comprises a monomer selected from the group consisting of
  - a) acrylic and methacrylic acid of the general formula  $H_2C=C(R^2)-C(O)OH$ ,
  - b) acrylates and methacrylates of the general formula  $H_2C=C(R^2)-C(O)OR^3$ ,
  - c) acrylamides and methacrylamides of the general formula  $(R^2)(R^2)C=C(R^2)-C(O)NHR^3$ ,
  - d) maleic and fumaric acid of the general formula  $HO(O)C-C(R^2)=C(R^2)-C(O)OH$ ,
  - e) maleates and fumarates of the general formula  $R^3O(O)C-C(R^2)=C(R^2)C(O)OR^3$ ,
  - f) vinyl ethers of the general formula  $(R^2)(R^2)C=C(R^2)-O-R^3$ ,
  - g) N-vinyl-2-pyrrolidone of the formula  $(R^2)(R^2)C=C(R^2)-N-CH_2-CH_2-CH_2-C(O)$ ,  


  - h) vinyl acetate of the general formula  $(R^2)(R^2)C=C(R^2)-OC(O)CH_3$ , and
  - i) aliphatic vinyl compounds of the general formula  $R^2CH=CHR^3$ , and mixtures thereof;
 where each  $R^2$  is independently hydrogen or  $C_1-C_{10}$  alkyl, and each  $R^3$  is independently an

aliphatic hydrocarbon group of up to about 10 carbon atoms that is substituted by one or more of carboxy, hydroxy, amino, or a (poly)ethylene oxide group optionally substituted by one or more sulfate, phosphate, or groups, or mixtures of such groups.

12. The process of Claim 11 wherein the monomer gas stream comprises a monomer selected from the group consisting of acrylic acid, methacrylic acid, hydroxyethylmethacrylate, methylmethacrylate, dimethylaminoethylmethacrylate, 2-hydroxyethylacrylate, N,N-dimethylacrylamide, N-acryloylmorpholine, ethylene glycol dimethacrylate, and mixtures thereof.

13. The process of any preceding claim wherein the gas of the monomer gas stream is ionized via pulsation of high frequency microwaves or radiowaves.

14. An absorbent article characterized in that said absorbent article comprises a durably wettable, liquid pervious topsheet produced by the processes of anyone of the preceding claims.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21710

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B05D7/24

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LEE S H ET AL: "PREPARATION AND CHARACTERIZATION OF THIN FILMS BY PLASMA POLYMERIZATION OF HEXAMETHYLDISILOXANE" THIN SOLID FILMS, CH, ELSEVIER-SEQUOIA S.A. LAUSANNE, vol. 325, no. 1/02, 18 July 1998 (1998-07-18), pages 83-86, XP000667948 ISSN: 0040-6090 figure 1 --- -/--	1



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/21710

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>TOSHIKI NAKANO ET AL: "ELECTRICAL PROPERTIES OF NITROGEN-CONTAINING PLASMA POLYMER FILMS"</p> <p>JOURNAL OF PHYSICS D. APPLIED PHYSICS, GB, IOP PUBLISHING, BRISTOL, vol. 23, no. 6, 14 June 1990 (1990-06-14), pages 711-718, XP000128879</p> <p>ISSN: 0022-3727</p> <p>the whole document</p>	1
A	<p>YOSHIMURA K ET AL: "PREPARATION OF HYDROPHILIC PLASMA-POLYMERS DERIVED FROM OXYGEN- CONTAINING ORGANIC MONOMERS"</p> <p>JOURNAL OF APPLIED POLYMER SCIENCE, US, JOHN WILEY AND SONS INC. NEW YORK, vol. 59, no. 6, 7 February 1996 (1996-02-07), pages 1033-1042, XP000551855</p> <p>ISSN: 0021-8995</p> <p>the whole document</p>	1, 11